Research Article

Functionalization of Carboxylated Multi-Wall Nanotubes with Derivatives of N1-(11H-Indeno[1,2-b]quinoxalin-11-ylidene)benzene-1,4-diamine

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Quinoxaline derivatives are compounds with pharmaceutical applications. In this study, derivatives of N1-(11H-indeno[1,2-b]quinoxalin-11-ylidene)benzene-1,4-diamine were synthesized and attached to carboxylated multi-wall nanotubes (MWNT-COOH). Functionalized carbon nanotubes were characterized by scanning electron microscopy (SEM) to study the shape of structures, transmission electron microscopy (TEM), fast Fourier transform infrared (FT-IR), Raman spectroscopy, and elemental analysis.

1. Introduction

Carbon nanotubes (CNTs) have unique properties that make them attractive for different engineering applications and many other fields [1]. Recently exploration of the biological and medical applications of CNTs has become a rapidly expanding field of research. In particular, the uses of CNTs as carriers of biologically active molecules are studied, such as drug delivery [2]. Multi-walled carbon nanotubes are more attractive than single-walled carbon nanotubes because of their relatively low production costs and availability in large quantities. However, because of their chemical inertness, carbon nanotubes have to be functionalized in order to acquire additional physicochemical properties [3]. These groups, which are chemically attached to the tubes, are mostly represented by -COOH groups, less by -C=O, and -OH groups [4-6]. Amidation of CNTs, can be done on the already carboxyl-functionalized nanotubes via treatment in octadecylamine (ODA). Amidation also can be done by first substituting a hydroxyl (-OH) group in a carboxylic (-COOH) group on chlorine by treatment in oxalyl chloride or SOCl₂ with the following addition of a long-chain

molecule of octadecyl amine [7, 8]. Compounds such as quinoxaline derivatives are an important class of benzoheterocycles which has received much attention in recent years owing to their both biological properties and pharmaceutical applications. These derivatives are particularly well known to antimicrobial [9], anticancer [10], antimalarial [11], anti-inflammatory [12], antinociceptive [13], antitubercular [14], anthelmintic [15], antidiabetic [16], and antiepileptic [17] properties. Carbon nanotubes can be used to deliver their cargoes to cells and organs. In this paper, we investigated, synthesis of MWNT-indenoquinoxalines, on the MWNT in addition to developing the amidation of MWNT with aromatic amine.

The products were characterized by FT-IR, SEM, TGA, TEM, and elemental analysis. Synthesis route of modified MWNT-COOH is shown in Figure 1.

2. Experimental

All reagents and solvents (oxalyl chloride, benzene-1,2-diamines, benzene-1,4-diamine, 1H-indene-1,2,3-trione, and

FIGURE 1: Synthesis route of modified MWNT-COOH.

FIGURE 2: Synthesis of derivatives of (11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine.

FIGURE 3: Preparation of MWNT-COCl.

DMF) were obtained from Merck Chemical Inc. (Darmstadt, Germany), and MWCNT-COOH (95% purity, 20–30 nm; Netvino Co. Ltd) were purchased and used as received. The FT-IR spectra were recorded using KBr tablets on a Nexus 870 FT-IR spectrometer (Thermo Nicolet, Madison, WI, USA). FT-Raman spectra were recorded on 960 ES, 1064 Thermo Nicolet. ¹H-NMR spectra were recorded on Bruker DRX-300 Avance spectrometer at solution in CDCl₃ using TMS as internal standard. SEM was used to study the morphology of the WCNTs. SEM measurement was carried out on the XL30 electron microscope (Philips, Amsterdam, Netherlands). TEM images were recorded using Philips EM 208. Elemental analyses of carbon, hydrogen, and nitrogen were

performed using a Series II 2400 (Perkin Elmer, Waltham, MA, USA).

2.1. Preparation Derivatives of (11H-Indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine. Equimolar quantities of benzene 1,2-diamine and indan-1,2,3 trione were refluxed in AcOH for 1 h at 100°C. Then 1 mmol benzene-1,4-diamine (4) were added to 11H-indeno[1,2-b]quinoxaline-11-one (3) and mixture was heated for three hours. Derivatives of (Z)-N1-(11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine (5) were filtered and washed with water and recrystallized from EtOH (Figure 2) [18].

2.1.1. The Desired Product 5. (11H-indeno [1,2-b] Quinoxaline-11-ylidene)benzene-1,4-diamine, was obtained in 85% yield, as dark violet, m.p > 220°C. IR: 3438 (N–H), 1619, 1596 (C=C), 1336, 1247 (C=N), and 727 (aromatic) cm⁻¹. 1H-NMR (DMSO-d₄) δ: 7.1–8.1 (m, 12 H, Ar-H), MS: *m/z* (%) = 320.

(8-Nitro-11H-indeno[1,2-b]quinoxaline-11-ylidene) benzene-1,4-diamine, was obtained in 89% yield, as dark violet, m.p > 220°C. IR: 3438 (N–H), 1619, 1596 (C=C), 1336, 1508 (NO₂), 1247 (C=N), and 727 (aromatic) cm⁻¹. 1H-NMR (DMSO-d₄) δ: 7.1–8.4 (m, 11 H, Ar-H), 4.2 (2H, NH₂), and MS: *m/z* (%) = 365.

2.2. Preparation of MWNT-COCl. 60 mg of the MWNT-COOH were sonicated in 90 mL of DMF for 40 min to give a suspension. Oxalyl chloride (2.5 mL) was added dropwise to the MWNT suspension at 0°C under N₂. The mixture was stirred at 0°C for 2 h and then at room temperature for another 2 h. Finally the temperature was raised to 70°C and the mixture was stirred overnight to remove excess oxalyl chloride. After cooling to room temperature, the mixture was filtered and washed thoroughly with EtOH [19] (Figure 3).

2.3. Preparation of MWNT-5. 150 mg of 5 dissolved in DMF was added to the 50 mg MWNT-COCl, and the mixture was stirred at 100°C for 48 h. Then the mixture was cooling to

FIGURE 4: Preparation of MWNT-5.

FIGURE 5: Fourier transform spectra of **A** MWNT-COOH, **B** MWNT-(11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine, and **C** MWNT-(8-nitro-11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine.

room temperature and filtered and washed to DMF and ethyl alcohol. Subsequently, the black solid was vacuum-dried at room temperature (Figure 4).

3. Results and Discussion

Elemental analyses of the modified MWNT **A**, **B**, and **C** are shown in Table 1. Apart from the carbon values, the atomic percentages of hydrogen and nitrogen of **B** and **C** (as compared with **A**) indicated that **A** is functionalized with (11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine, and (8-nitro-11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine.

Figure 5 shows the FT-IR spectrum of the modified MWNTs. In spectrum **A**, the band at around 1527 cm⁻¹ corresponds to the stretching mode of the C=C double bond that forms the framework of the carbon nano tube sidewall [20]. The peaks at 1704, 3304 cm⁻¹, and 1071 cm⁻¹ apparently corresponds to the stretching modes of the carboxylic acid groups [21, 22]. In spectrum **B**, the new strong peak at 3439–3500 cm⁻¹ can be assigned to the N–H stretching

TABLE 1: Elemental analysis of **A** carboxylated multiwalled carbon nanotubes and **B** (11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine multiwalled, **C** (8-nitro-11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine.

Sample	%C	%H	%N
A	96.40	0.04	0
B	86.92	2.21	3.23
C	81.47	2.01	4.02

modes. The carbonyl peak in the spectrum **B** shift to 1657 cm⁻¹ (as compared with 1704 cm⁻¹ in spectrum **A**) is a result of amide (C=O)NH linkage formation. In the spectrum **C**, strong peak at 1647 cm⁻¹ is a result of amide group (C=O)NH and two peak in the range of 1393 and 1517 cm⁻¹ are for (NO₂) group.

The morphology of the resulting MWNT-5 was observed with SEM. In Figure 6, SEM images of **A**, **B**, **C** are shown. It indicates that the MWNT-COOH (**A**) has a smooth surface. The changes in the morphology for **B** and **C** are remarkable.

FIGURE 6: Scanning electron microscopy images of (a) MWNT-COOH, (b) MWNT- (11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine, and (c) MWNT- (8-nitro-11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine.

FIGURE 7: TEM images of (a) MWNT-COOH, (b) MWNT- (11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine, and (c) MWNT- (8-nitro-11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine.

A uniform tubular layer due to amide group on the surface of the MWNT (the rough part) is observable. It seems that the diameters of **B, C** are slightly increased in comparison to **A**.

The TEM images of the MWNT-COOH (**A**) and the MWNT-indenoquinoxaline derivatives (**B, C**) are compared in Figure 7. The MWNT-COOH seemed to be a bundle or a rope of MWNT. However, the dissociation of the bundles was observed in the MWNT-indenoquinoxaline derivatives. Functionalization prevented MWNT to aggregate in the form of bundles and enhanced their dispersibility. So, the MWNT-indenoquinoxaline derivatives showed a high and facile dispersion in solvents than the MWNT-COOH did. The TEM images revealed that the functionalization of MWNT-COOH with indenoquinoxaline derivatives retained the nature of MWNT-COOH even after the functionalization, without destroying their original electronic structure and behavior. It can be concluded that the amount of functional groups introduced on MWNT-COOH was not large enough to destroy the structure of MWNT-COOH.

Raman spectroscopy is a powerful tool used to provide structural information about MWNT-COOH before and after functionalization. As shown in Figure 8, the D and G bands of the MWNT at around 1339 and 1596 cm, attributed

to defects, disorder-induced peaks, and tangential-mode peaks (**A–C**) can be clearly observed for MWNT-COOH and MWNT-indenoquinoxaline derivatives. Additionally, the intensity ratio (I_D/I_G) of the D and G bands for MWNT-(11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine (**B**) is 1.46 and MWNT- (8-nitro-11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine (**C**) is 1.35, which is greater than that for MWNT-COOH (**A**) 0.54. The increase in intensity of the defect mode at 1339 cm was related to sp^3 hybridization of carbon and is used as an evidence of the disruption of the aromatic system of π electrons by the attached molecules [23–26].

As a result of this functionalization, the solubility of MWNT-indenoquinoxaline derivatives was improved significantly, and they were easily dispersed in DMF. A dispersion test gives a fair idea whether the modification on the carbon nanotubes has been achieved or not. Figure 9 presents a photograph of three vials containing MWNT-COOH and MWNT-indenoquinoxaline derivatives dispersed in DMF. As can be seen from Figure 8, MWNT-COOH are insoluble in DMF, while the modified CNTs can be directly dispersed in DMF (without sonication) homogeneously and no precipitation was found even after it was sealed for 1 month at room temperature.

(a)

(b)

(c)

FIGURE 8: Raman spectroscopy of (a) MWNT-COOH, (b) MWNT- (11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine, and (c) MWNT- (8-nitro-11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine.

FIGURE 9: The images of **A** MWNT-COOH, **B** MWNT-(11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine, and **C** MWNT-(8-nitro-11H-indeno[1,2-b]quinoxaline-11-ylidene)benzene-1,4-diamine in DMF (1 mg/6 mL) after standing for 1 month.

4. Conclusions

The chemistry of MWNTs offers considerable scope for development of functional materials, structures, and devices based on MWNTs. A detailed methodology for the modification and functionalization of multi-walled carbon nanotube (MWNT) via amidation has been presented. We have introduced indenoquinoxaline derivatives onto the surface of nanotubes. The functionalized MWNTs were demonstrated by SEM images, FT-IR, Raman spectroscopy, and elemental analysis. The results show successful functional groups.

Acknowledgments

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